* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]a hard carbon film sliding member [low friction / this invention] -- especially -- an engine oil and a truss -- it is related with a low friction hard carbon film sliding member suitable for being used in lubricating oils, such as mission oil, and a manufacturing method for the same.
[0002]
[Description of the Prior Art]A hard carbon coat is amorphous-like a carbon film or a hydrogenated carbon film, and is also called a-C:H (amorphous carbon or hydrogenation amorphous carbon), i-C (eye carbon), and DLC (diamond like carbon or Dee Elsie).
[0003]Vapor phase synthetic methods, such as an ion-beam-deposition method using the plasma CVD method which carries out plasma decomposition of the hydrocarbon gas, and forms membranes or carbon, and a hydrocarbon ion, are used for the formation. This hard carbon coat is high hardness, and it is smooth, and the surface is excellent in abrasion resistance, and has further the low friction performance which was excellent in the low friction coefficient from that solid lubrication nature. And the coefficient of friction under-less lubricous of a hard carbon coat is about 0.1 to the coefficients of friction under the usual smooth steel-materials surface being-less lubricous being 0.5-1.0.
[0004]Now, taking advantage of these outstanding characteristics, the application to working jigs, such as cutting tools including the edge of a drill and a grinding tool, a plastic-working public-funds type and a valve cock, the moving part under [like a capstan roller]-less lubricous, etc. is measured.
[0005]Also in machine parts, such as an internal-combustion engine which slides in a lubricating oil, the demand of liking to reduce a mechanical loss as much as possible from the field of energy expenditure or an environmental problem is increasing, and by the severe part

of the large sliding condition of friction loss especially. Low friction-ization by the hard carbon coat which has these solid lubrication nature is desired.

[0006]

[Problem(s) to be Solved by the Invention]however -- coating a slide member with the above-mentioned hard carbon coat -- engine oil and a truss -- it becoming a certain amount of low friction from the smooth nature, when it is made to slide in lubricating oils, such as a missions oil, but. The problem that only low friction performance equivalent to the slide member which carried out hard coat processing in which it did not have other solid lubrication nature, for example, the slide member which performed ion plating coat processing of titanium nitride (TiN) and chromium nitride (CrN), was shown became clear.

[0007]That is, in the conventional slide member by which hard carbon coat processing was carried out, although there was solid lubrication nature, in the lubricating oil, the problem that only friction performance equivalent to the coat processing slide member which is equivalent surface roughness and does not have solid lubrication nature, or the steel members by which super-finishing processing was carried out was shown became clear.

[0008]For example, three 3/8-inch balls are pushed by the load of 1kgf in a lubricating oil, When it lets it slide in the relative velocity of 0.03 m/sec, the coefficients of friction of the diamond like carbon which is a hard carbon coat are 0.08-0.12, Compared with the steel material and chromium nitride (CrN) ion-plating-treatment film which are equivalent surface roughness and do not carry out coat processing, it is an equivalent coefficient of friction in a lubricating oil.

[0009]In lubricating oils, such as engine oil and a transmission oil, Although many moving parts which processed on the surface the molybdenum disulfide (MoS_2) which has solid lubrication nature so that with a coefficient of friction of mu= 0.07 or less low friction may be realized, and polytetrafluoroethylene (PTFE) are also made, application already, When used by the still severer sliding condition under high planar pressure, abrasion resistance ran short and the performance could be attained in the first stage, but when long term use was carried out, it wore out, and the performance had the problem of being unmaintainable.

[0010]

[Objects of the Invention]The slide member which processed the hard carbon coat which this invention is made [coat] paying attention to these problems, and made the surface contain nitrogen and/or oxygen, Or even if it is among a lubricating oil, the solid lubrication nature works effectively, and it aims at providing the slide member which was excellent in abrasion resistance with the coefficient of friction at mu= 0.07 or less low friction because a hydrogen content considers it as the slide member which processed the hard carbon coat not more than 10at%.

[0011]

[Means for Solving the Problem]Although there is almost no report and it is the translation which had many questions about the friction characteristic of a hard carbon coat in inside of a lubricating oil, Consider wholeheartedly influence which it has on the friction characteristic in inside of nitrogen contained in a hard carbon coat, oxygen, and a lubricating oil of hydrogen concentration in this invention, and this is clarified, When concentration of nitrogen of a hard carbon coat which can realize low friction in lubricating oil, oxygen, and hydrogen specified, it succeeded in the coefficient-of-friction value mu in inside of a lubricating oil realizing 0.07 or less low friction performance.

[0012]That is, in a slide member used in a lubricating oil, a surface layer consists of a hard carbon coat at least, and a slide member concerning this invention is characterized by making the hard carbon coat surface contain nitrogen and/or oxygen, as indicated to claim 1.

[0013]Similarly, in a slide member used in a lubricating oil, a hard carbon film sliding member concerning this invention is characterized by a surface layer's consisting of a hard carbon coat at least, and a surface hydrogen content consisting of a hard carbon coat not more than 10at%, as indicated to claim 2.

[0014]And in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 3, it is characterized by a hard carbon coat being a vapor-phase-synthesis diamond.

[0015]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 4, it is characterized by nitrogen and/or an oxygen content of the hard carbon coat surface being more than 0.5at%.

[0016]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 5, it is characterized by nitrogen and/or an oxygen content of the hard carbon coat surface being less than 30at%.

[0017]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 6, it is characterized by nitrogen and/or an oxygen content of the hard carbon coat surface being less than more than 4at%20at%.

[0018]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 7, it is characterized by surface roughness being less than Ra0.1micrometer.

[0019]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 8, it is characterized by surface hardness being 1000 or more Hv(s).

[0020]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 9, it is characterized by thickness of a hard carbon coat being 1 micrometers or more 10 micrometers or less, and a coefficient of friction in inside of a lubricating oil being 0.07 or less.

[0021]Similarly, in an embodiment of a hard carbon film sliding member concerning this invention, as indicated to claim 10, it is characterized by constituting adjusting SIMM of a valve gear of an internal-combustion engine.
[0022]A manufacturing method of a hard carbon film sliding member concerning this invention, As indicated to claim 11, after facing manufacturing the hard carbon film sliding member according to any one of claims 1 to 10 and coating a base material surface with a hard carbon coat by vapor phase synthesis, it is characterized by plasma treatment or carrying out an ion implantation.
[0023]
[Function of the Invention]Since the hard carbon film sliding member concerning this invention is considered as the above-mentioned composition, Since many polar groups can be made to exist in the surface, it will physisorb, or will be easy to chemisorb, the oily additive agent contained in a lubricating oil will become the surface, and mu= 0.07 or less low friction hard carbon film sliding member will be obtained in a lubricating oil.
[0024]And since it will become a tendency which runs short of the abrasion resistance under high planar pressure if it becomes the tendency for the low friction in the inside of the lubricating oil described above when there were few surface nitrogen and/or oxygen densities than 0.5at% to be hard to realize and increases more than 30at% on the contrary, it is preferred to make 30at% into a maximum. And it is suitable in order to be able to obtain the low friction characteristic in the inside of a lubricating oil, without considering it as 4at% - 20at% still more preferably spoiling abrasion resistance and smooth nature.
[0025]Plasma treatment which makes the surface contain nitrogen and/or oxygen can be carried out using a device as shown in drawing 2.
[0026]That is, the plasma treatment apparatus 21 shown in drawing 2 offers the vacuum chamber 22, the substrate holder 24 for holding the substrate 23 which constitutes a slide member is offered on the internal lower part of this vacuum chamber 22, and this substrate holder 24 is connected to the bias power supply 25. Have formed RF electrode 26 above the substrate 23, and RF power 27 is connected to this RF electrode 26, and it enables it to have supplied the plasma formation gas in the gas bomb 28 through the gas mass flow regulator 29. And the discharge plasma 30 is formed between RF electrodes 26, and the ion 32 is formed in the portion of the aperture 31, it is made to have reached the substrate 23 and the radical ion beam 33 makes the vacuum chamber 22 the thing in which evacuation is possible via the vacuum pump in the direction of arrow A. And it can make as [carry / in RF supplied power:10-100W, gas mass flow:5 - 50 cc/min, bias voltage:-250 - +250V], using such a plasma treatment apparatus 21.
[0027]On the other hand, although detection is dramatically difficult about hydrogen concentration, low friction in the inside of a lubricating oil comes to be carried out by realization

by making that it is less than hydrogen content 10at%. And in order to use less than hydrogen content 10at%, It is preferred that it shall be the hard carbon film sliding member which coated diamond polycrystal membrane with the amorphous carbon film manufactured by the carbon ion beam method not to use hydrocarbon gaseous plasma at least at the time of membrane formation etc., or the heat CVD method.

[0028]As for surface roughness, it is preferred to use less than Ra0.1micrometer in consideration of the low friction characteristic and the partner aggression, and, as for surface hardness, it is preferred to be referred to as 1000 or more Hv(s) which can secure abrasion resistance. As for thickness, since adhesion strength may be insufficient if thinner than 1 micrometer, the remaining stress in a film may become large when thicker than 10 micrometers, and it may exfoliate automatically about thickness further again, it is desirable to be 1-micrometer or more referred to as 10 micrometers or less.

[0029]As for such a hard carbon film sliding member, it is also preferred to, constitute the adjusting SIMM of the valve gear of an internal-combustion engine for example, if needed.

[0030]

[Effect of the Invention]According to the slide member concerning this invention, as indicated to claim 1, In the slide member used in a lubricating oil, a surface layer consists of a hard carbon coat at least, Since the hard carbon coat surface was made to contain nitrogen and/or oxygen and it is possible to operate the solid lubrication nature effectively even if it is among a lubricating oil, The effect which becomes in work size that it is possible to provide the hard carbon film sliding member of a super-life excellent in lubricity and abrasion resistance is brought about.

[0031]In the slide member used in a lubricating oil as indicated to claim 2, Since a surface layer shall consist of a hard carbon coat at least, a surface hydrogen content shall consist of a hard carbon coat not more than 10at% and it is possible to operate the solid lubrication nature effectively even if it is among a lubricating oil, The effect which becomes in work size that it is possible to provide the hard carbon film sliding member of a super-life excellent in abrasion resistance is brought about.

[0032]And as indicated to claim 3, when a hard carbon coat shall be a vapor-phase-synthesis diamond, the effect which becomes in work size that it is possible to provide the hard carbon film sliding member which was smooth in the surface with high hardness, and was excellent in abrasion resistance is brought about.

[0033]As indicated to claim 4, when nitrogen and/or the oxygen content of the hard carbon coat surface shall be more than 0.5at%, the effect which becomes in work size of becoming what is produced by stabilizing more the low friction in the inside of a lubricating oil is brought about.

[0034]As indicated to claim 5, when nitrogen and/or the oxygen content of the hard carbon

coat surface shall be less than 30at%, the effect which becomes in work size that it is possible for it to be stabilized more and to make abrasion resistance under high planar pressure into sufficient thing is brought about further again.

[0035]As indicated to claim 6, when nitrogen and/or the oxygen content of the hard carbon coat surface shall be less than more than 4at%20at%, further again, The low friction in the inside of a lubricating oil is obtained by being stabilized further, and the effect which becomes in work size that it is possible to provide the hard carbon film sliding member which the abrasion resistance under high planar pressure was stabilized further, and made sufficient thing is brought about.

[0036]As indicated to claim 7, when surface roughness shall be less than Ra0.1micrometer, it is made to a low friction thing further again, and the effect which becomes in work size that the partner aggression is made to a small thing is brought about.

[0037]As indicated to claim 8, when surface hardness shall be 1000 or more Hv(s), the effect which becomes in work size that it is possible to also fully have secured abrasion resistance is brought about further again.

[0038]As indicated to claim 9, when the thickness of a hard carbon coat shall be 1 micrometers or more 10 micrometers or less and the coefficient of friction in the inside of a lubricating oil shall be 0.07 or less, further again, Density intensity to a substrate can be made good, and the effect which becomes in work size that it is possible to provide the low friction sliding member which was excellent in the endurance which can make the remaining stress in a film small and can abolish fear of exfoliation is brought about.

[0039]As indicated to claim 10, the effect which becomes in work size that it is possible to make the mechanical loss in a valve gear small is brought about further again by making with what constitutes the adjusting SIMM of the valve gear of an internal-combustion engine.

[0040]In the manufacturing method of the hard carbon film sliding member concerning this invention. As indicated to claim 11, it faces manufacturing the hard carbon film sliding member according to any one of claims 1 to 10, the plasma treatment after coating a base material surface with a hard carbon coat by vapor phase synthesis -- or, since it was made to carry out an ion implantation, Even if it is among a lubricating oil, the effect which becomes in work size that it is possible to manufacture the hard carbon film sliding member excellent in the lubricity and abrasion resistance which can operate the solid lubrication nature effectively is brought about.

[0041]

[Example]It cannot be overemphasized that this invention is not hereafter limited only to such an example although the example of this invention is described in detail with a comparative example.

[0042]In the slide member 1 as shown in drawing 1, the hard carbon coat 3 was coated on

diameter:30mm and the 4-mm thickness:disk substrate 2, and the rubbing test was done with the specimen using this slide member 1. The slide member 1 which constitutes this specimen should form the hard carbon coat 3 on the disk substrate 2 by specification as shown in Table 1.

[0043](Example 1) Example 1 deposits a vapor-phase-synthesis diamond coat by a thickness of 10 micrometers with a heat CVD method on the ceramic disk substrate which consists of silicon nitride, and, subsequently carries out polishing work of this diamond coat surface with a diamond wheel or an abrasive grain, The slide member to which surface roughness Ra0.05micrometer was made was produced.

[0044](Example 2) After Example 2 carries out super-finishing processing of the surface of the steel substrate which consists of steel for carburization (JIS SCN415) at Ra0.04micrometer, The hard carbon coat was coated with the ion plating method using a carbon ion beam, and the slide member of surface roughness Ra0.09micrometer was produced as what has nothing finish-machining after membrane formation.

[0045](Example 3) Example 3 should carry out lap processing of the surface of the slide member of Example 2, and should make surface roughness Ra0.03micrometer to it.

[0046](Example 4) After Example 4 carries out super-finishing processing of the surface of the steel substrate which consists of steel for carburization (JIS SCN415) at Ra0.04micrometer, After forming a diamond like carbon (DLC) film on a substrate using hydrocarbon gas with a plasma CVD device, the film which made the surface contain oxygen using the plasma treatment apparatus further shown in drawing 2 was produced. At this time, oxygen plasma treatment was carried out on condition of RF supplied power:50W, gaseous oxygen flow rate:10 cc/min, and bias voltage:-100V. The oxygen content of the hard carbon coat surface obtained by this was about 3.5 at(s)%.

[0047](Example 5) Let Example 5 be the slide member which carried out the same plasma oxygenation as Example 4 to the hard carbon coat member of Example 3. The oxygen content of the hard carbon coat surface obtained by this was about 3.5 at(s)%.

[0048](Example 6) Example 6 should carry out nitrogen plasma processing, and performed plasma treatment conditions to the diamond polycrystal membrane of Example 1 on the same conditions as Examples 4 and 5. The oxygen content of the hard carbon coat surface obtained by this was about 5.7 at(s)%.

[0049](Comparative example 1) The comparative example 1 carries out manganese phosphate salt processing, after carrying out the grinding process of the surface of the substrate which consists of steel for carburization (JIS SCN415) to Ra0.24micrometer.

[0050](Comparative example 2) The comparative example 2 carries out super-finishing processing of the surface of the substrate which consists of steel for carburization (JIS SCN415) at Ra0.04micrometer.

[0051](Comparative example 3) The comparative example 3 coats the slide member of the comparative example 2 with the chromium nitride (CrN) coat of hardness Hv1500 which has 2.0-micrometer thickness by the ion plating method further.
[0052](Comparative example 4) The comparative example 4 is what formed diamond polycrystal membrane on the silicon nitride substrate with the heat CVD method, and surface roughness is Ra0.12micrometer.
[0053](Comparative example 5) The comparative example 5 forms a diamond like carbon (DLC) film on a substrate using hydrocarbon gas with a plasma CVD device, after carrying out super-finishing processing of the surface of the substrate which consists of steel for carburization (JIS SCN415) at Ra0.04micrometer.
[0054](Comparative example 6) The comparative example 6 carries out hard carbon coat coating by the ion plating method using a carbon ion beam, after carrying out the grinding process of the surface of the substrate which consists of steel for carburization (JIS SCN415) to Ra0.20micrometer. And the surface roughness of the coat after the membrane formation in this case is a thing of Ra0.25micrometer.
[0055](Comparative example 7) Let the comparative example 7 be the slide member which carried out the same plasma oxygenation as Example 4 to the hard carbon coat member of the comparative example 6. The oxygen content of the hard carbon coat surface obtained by this was about 40 at(s)%.
[0056](Example of an examination) In doing a rubbing test, the coefficient of friction was measured using the frictional testing machine 41 of a pin one disk type as shown in drawing 3 as a friction test device.
[0057]The work table 43 which was supported as for this friction test device 41 enabling the free rotation to the axis of rotation 42 is arranged, The slide member 1 which is a specimen is installed in this work table 43, and the 3/8-inch ball 44 made from SUJ2 for bearings is arranged three pieces to the upper surface side of this slide member 1, and it is constituted so that it may push by load 1.0kgf with the spring 45.
[0058]And the ball 44 is being fixed, respectively so that it cannot rotate to the ball holder 46, The torque according to the frictional force which the axis of rotation 42 is connected with the motor 47, rotates with the relative sliding velocity of 0.01-0.1 m/sec to the ball 44, and generates between the ball 44 and the specimen slide member 1 shall be measured by the load cell 48, and the coefficient of friction shall be computed. It is set up so that the specimen slide member 1 may be immersed into the lubricating oil 49, and an oil temperature may be 80 ** by the oil-temperature control unit which the oil bath tub 50 is installed and is not illustrated. As the lubricating oil 49, it carried out using commercial engine-oil 5W-30SG.
[0059]And the slide member of each example and comparative example which are shown in Table 1 is arranged as the specimen slide member 1 of the frictional testing machine 41, and

the result of having measured the coefficient of friction in the lubricating oil 49 is shown. The result of having measured the lubricating oil on the load also with same coefficient of friction and the sliding-velocity conditions under-less lubricous when it was not able to go into an oil bath tub is shown as reference. The test condition at this time was performed in load load:1kgf to the three balls 44, and sliding-velocity:0.25m/sec (250 rpm).

[0060]

[Table 1]

区分		基材	皮膜処理	成膜法	膜厚 (μm)	硬度 (Hv)	表面粗さ Ra (μm)	備考	摩擦係数μ 無潤滑	摩擦係数μ 潤滑油中	区分	
実施例	1	窒化珪素	ダイヤモンド多結晶膜	熱CVD法	10.0	−	0.05	10at%>水素	0.080	0.058	1	実施例
	2	浸炭用鋼	硬質炭素膜（a−C）	イオンプレーティング法	2.0	3500	0.09	10at%>水素	0.110	0.065	2	
	3	浸炭用鋼	硬質炭素膜（a−C）	イオンプレーティング法	2.0	3500	0.03	10at%>水素	0.090	0.066	3	
	4	浸炭用鋼	ダイヤモンドライクカーボン膜（DLC）	プラズマCVD法	1.0	2500	0.04	プラズマ酸素処理, 3.5at%酸素, 10at%<水素	0.098	0.056	4	
	5	浸炭用鋼	硬質炭素膜（a−C）	イオンプレーティング法	2.0	3500	0.04	プラズマ酸素処理, 3.5at%酸素, 10at%>水素	0.095	0.059	5	
	6	窒化珪素	ダイヤモンド多結晶膜	熱CVD法	10.0	−	0.05	プラズマ窒素処理, 5.7at%窒素, 10at%>水素	0.080	0.049	6	
比較例	1	浸炭用鋼	リン酸マンガン塩処理	化成処理	10.0	−	1.50		1.080	0.125	1	比較例
	2	浸炭用鋼	無し	−	−	720	0.04		0.480	0.096	2	
	3	浸炭用鋼	窒化クロム（CrN）	イオンプレーティング法	2.0	1500	0.07		0.380	0.108	3	
	4	窒化珪素	ダイヤモンド多結晶膜	熱CVD法	10.0		0.12	10at%>水素	0.090	0.075	4	
	5	浸炭用鋼	ダイヤモンドライクカーボン膜（DLC）	プラズマCVD法	1.0	2500	0.04	10at%<水素	0.098	0.099	5	
	6	浸炭用鋼	硬質炭素膜（a−C）	イオンプレーティング法	2.0	3500	0.25	10at%>水素	0.125	0.085	6	
	7	浸炭用鋼	硬質炭素膜（a−C）	イオンプレーティング法	2.0	3500	0.05	プラズマ酸素処理, 40at%酸素, 10at%>水素	剥離	0.100	7	

[0061]A hard carbon coat is low compared with the comparative example 1 and the comparative example 3 which processed the coat without the comparative example 2 and solid lubrication nature in which a coefficient of friction does not have a coat by the solid lubrication nature under-less lubricous so that the measuring result of the coefficient of friction shown in Table 1 may show.

[0062]However, in a lubricating oil, the diamond like carbon film of the comparative example 5 containing more hydrogen than 10at% is a coefficient of friction equivalent to the comparative example 1 and the comparative example 2 without coat processing.

When surface roughness becomes more than Ra0.10micrometer, a coefficient of friction

becomes 0.07 or more, and the friction reduction effect also has few the diamond polycrystal membrane and the amorphous carbon films of the comparative example 4 whose content of hydrogen is less than 10at%.

[0063]On the other hand, it turns out that the content of hydrogen contains nitrogen and oxygen on less than 10at% and/or the surface, and it can reduce friction loss effectively by Ra even if each coefficient of friction is 0.07 or less and surface roughness is among a lubricating oil in Examples 1-6 of 0.10 micrometer or less.

[0064]Even the cam at the time of using for the adjusting SIMM of the valve gear of an internal-combustion engine as shows drawing 4 the carbon hard-anodic-oxidation-coatings member of Example 5 measured the friction loss torque of the hit. And torque measurement was measured with the torque meter attached to the cam-shaft axis which is not illustrated.

[0065]In the valve gear of the internal-combustion engine which shows drawing 4, the cam-shaft axis 52 which offered the cam 51 is rotated by the timing belt which is not illustrated. And the valve 53 is inserted in the valve guide 54, and the valve lifter 55 is installed above the axis end of the valve 53. And the valve spring 57 was fixed to the valve 53 by the retainer 58 and the cotter 59 between the cylinder head 56 and the valve lifter 55, and load is added in the direction which closes the valve 53. Adjusting SIMM 60 fits in above the valve lifter 55, It is adjusted by the thickness of adjusting SIMM 60 so that clearance with the cam 51 may be set to about 0.3 mm, and when the cam-shaft axis 52 drives, the cam 51 rotates and it has become a mechanism in which the valve 53 is made to move reciprocately in slide contact with adjusting SIMM 60.

[0066]A test condition shall be made into cam shaft number-of-rotations:300rpm (at the time of an idling), spring Max load:50kgf, and engine-oil-temperature:80 **, the surface roughness of the partner cam 51 which ****s to adjusting SIMM 60 shall perform super-finishing processing, and Ra0.05micrometer shall be made.

[0067]The slide member of the comparative example 1 and the comparative example 2 currently used conventionally besides the above-mentioned Example 5 for comparison, The loss torque at the time of using for adjusting SIMM 60 similarly also measured the slide member of the comparative example 3 which carried out chromium nitride film processing, and the slide member of the comparative example 5 which carried out hard carbon coat processing on the conditions. The measured result is shown in drawing 5.

[0068]Also in the same surface roughness, the adjusting SIMM of Example 5 had small friction loss torque compared with the comparative example, and having excelled in friction performance was admitted so that the result shown in drawing 5 might show.

[Translation done.]